



## Size effect on SrRuO<sub>3</sub>/BaTiO<sub>3</sub>/SrRuO<sub>3</sub> ferroelectric ultrathin film capacitor

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### ABSTRACT

We have carried out a detailed investigation on the size effect on SrRuO<sub>3</sub>/BaTiO<sub>3</sub>/SrRuO<sub>3</sub> ferroelectric ultrathin film capacitors with film thickness fully strained with a SrTiO<sub>3</sub> substrate. We employ the transverse field Ising model, taking into account the incomplete charge compensation of the realistic SrRuO<sub>3</sub> electrode and the misfit strain imposed by the SrTiO<sub>3</sub> substrate in the Hamiltonian, to quantitatively explain the experimental observation in the literature. It is found that BaTiO<sub>3</sub> ultrathin films between two metallic electrodes lose their ferroelectric properties below a critical thickness of about 4.17 nm due to the enhancement of the quantum effect under the influence of the incomplete charge compensation of the electrode.

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### 1. Introduction

Ferroelectric thin films continue to be the subject of intensive experimental and theoretical research due to their numerous applications in microelectronics [1,2]. The current trend of ferroelectric (FE) device miniaturization makes investigations of the size effect on ultrathin FE films especially important. Many FE-based electronic devices have the capacitor configuration with an FE layer inserted between two conducting electrodes, which makes the bound charges at the surfaces of the FE layer compensated by free charge carriers in the conducting electrodes. The crucial physics with a realistic electrode is incomplete compensation of the FE polarization charge: the compensation charges will be induced with a finite extent, called the Thomas–Fermi screening length  $\lambda$ . Such an incomplete compensation of the polarization charges will induce a depolarizing field  $E_d$  in the FE layer with a direction opposite to that of the FE polarization  $P$  normal to the surface and consequently suppress the FE polarization [3].  $E_d$  produced by the incomplete screening of the bound polarization charge has been known to play a dominant role in determining the critical thickness [4] and the domain structure of ultrathin FE films [5–7].

Recently, Junquera and Ghosez [4] performed first principles calculations for a fully strained SrRuO<sub>3</sub> (SRO)/BaTiO<sub>3</sub> (BTO)/SRO

heterostructure on a SrTiO<sub>3</sub> (STO) (001) substrate. By taking into account the depolarizing field  $E_d$ , they showed that the polarization of the BTO thin film decreases with decreasing film thickness and vanishes at the critical thickness of 2.4 nm. More recently, Kim et al. [8,9] have published a series of experimental studies of ultrathin, down to 5 nm, FE SRO/BTO/SRO capacitors fully strained with an STO substrate. They demonstrated the effect of  $E_d$  on the FE polarization for BTO films with various film thickness from 5 to 30 nm and provided an upper bound of 5 nm for the critical thickness.

Early experimental and theoretical researches mainly focused on the intrinsic size effect [10–12]. Up to now, most theoretical research did not take into account the extrinsic effect, including such characteristics as the finite screening length  $\lambda$  of the electrode and the strain conditions imposed by the substrate, on the FE polarization. We propose in the present letter an appropriate model to quantitatively describe the influence of a realistic electrode and substrate, and demonstrate the size effect on an SRO/BTO/SRO FE ultrathin film capacitor fully strained with an STO substrate.

The Landau theory and transverse field Ising model (TIM) are the two most frequently used approaches to treat the ferroelectric characteristics. In comparison with the Landau theory for classical cases, the TIM is an order–disorder model treating the interactions of dipole moments, as well as the quantum mechanical effects within a unified framework. The TIM has been extended successfully to ultrathin FE films [13] and Ba<sub>x</sub>Sr<sub>1–x</sub>TiO<sub>3</sub> FE solid solutions [14] to investigate their phase transition properties. In the present work, we employ the TIM to investigate the size

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effect on a fully strained SRO/BTO/SRO FE ultrathin film capacitor on an STO substrate, which induces a compressive strain in the film, by taking into account the depolarizing field induced by the incomplete screening of the bound polarization charge at the FE–electrode interface.

## 2. Theoretical background

The Hamiltonian of the system can be expressed as

$$H = - \sum_i \Omega S_i^x - \frac{1}{2} \sum_{i,j} J_{i,j} S_i^z S_j^z - 2 \sum_i (E + E_d) \mu S_i^z, \quad (1)$$

where the intrinsic surface effect [11] on the polarization is neglected for clarity,  $\Omega$  is the tunneling frequency to scale the quantum effect,  $S_i = \frac{1}{2}$  and  $-\frac{1}{2}$  for up and down pseudospins, respectively,  $i \neq j$ ,  $J_{ij}$  denotes the nearest-neighbor pseudospin interaction,  $E$  represents the external electric field,  $\mu = 2.35 \text{ e}\text{\AA}$  is the effective dipolar moment of each spin that we obtained by fitting the experimental data in Ref. [8], and the summation  $\sum_j J_{ij} = J$  covers the nearest neighbors of site  $i$ .  $E_d = -\frac{P}{\epsilon_0 \epsilon_F} \left( \frac{2\epsilon_F/d}{2\epsilon_F/d + \epsilon_e/\lambda} \right)$  [3,8] is the depolarizing field due to the incomplete charge compensation, where  $d$  is the film thickness, and accurate values of the parameters  $\epsilon_0$ ,  $\epsilon_e$ ,  $\epsilon_F$ , and  $\lambda$  can be found in Ref. [8].

In our treatment of the size effect in a fully strained BTO ultrathin film capacitor ( $d \leq 30 \text{ nm}$ ) within the framework of the TIM, we not only take into account the depolarizing field, but also the compressive misfit strain  $\epsilon_s = (a_{\parallel} - a_0)/a_0$ , where  $a_0 = 0.4005 \text{ nm}$  [15] is the lattice constant of free-standing cubic BTO and  $a_{\parallel} = 0.3905 \text{ nm}$  [9] is the in-plane lattice parameter of a fully strained BTO film, resulting in the misfit strain  $\epsilon_s$  being  $-2.5\%$ . Choi et al. [16] reported the enhancement of ferroelectricity in strained BTO thin films, in which  $T_C$  is enhanced by the compressive strain via  $T_C = \theta + A\epsilon_s$ . Here,  $\theta = 393 \text{ K}$  is the Curie–Weiss temperature of unstrained BTO and  $A$  is a constant associated with Curie constant, electrostrictive coefficients and elastic compliances [16]. By fitting the experimental results [16] of thick BTO films grown by pulsed laser deposition (PLD) with various strains, we obtain  $A = -320 \text{ K}$  and  $T_C = 1193 \text{ K}$  for  $30 \text{ nm}$  BTO thin film. We can therefore get  $J = 6127k_B \text{ K}$  and  $\Omega = 1850k_B \text{ K}$ , which are different from the corresponding parameters for bulk BTO [17], by fitting the experimental spontaneous polarization for  $d = 30 \text{ nm}$  in Ref. [8].

We therefore can apply the mean field approximation on a single ion in dealing with the Hamiltonian  $H$  and obtain the numerical results of several physically important quantities related to the ferroelectric properties in BTO ultrathin film capacitor as

$$P = 2N\mu \langle S^z \rangle = 2N\mu \frac{\text{Tr} S^z \exp(-\beta H)}{\text{Tr} \exp(-\beta H)} = \frac{N\mu (J_d P + 4N\mu^2 E)}{\sqrt{4N^2\mu^2\Omega^2 + (J_d P + 4N\mu^2 E)^2}} \times \tanh \frac{\sqrt{4N^2\mu^2\Omega^2 + (J_d P + 4N\mu^2 E)^2}}{4N\mu k_B T}, \quad (2)$$

$$\chi(T, d) = \frac{1}{\epsilon_0} \left. \frac{dP}{dE} \right|_{E=0}, \quad (3)$$

where  $N$  is the pseudospin density [18],  $\langle S^z \rangle$  is the average of the pseudospin proportional to the electrical polarization,  $\beta = (k_B T)^{-1}$ , and  $\chi(T, d)$  is the dielectric susceptibility. It should be noted that  $J_d = J - \frac{8N\mu^2\lambda}{\epsilon_0(\epsilon_e d + 2\epsilon_F\lambda)}$  is the modified nearest-neighbor pseudospin interaction due to the effect of incomplete charge compensation.

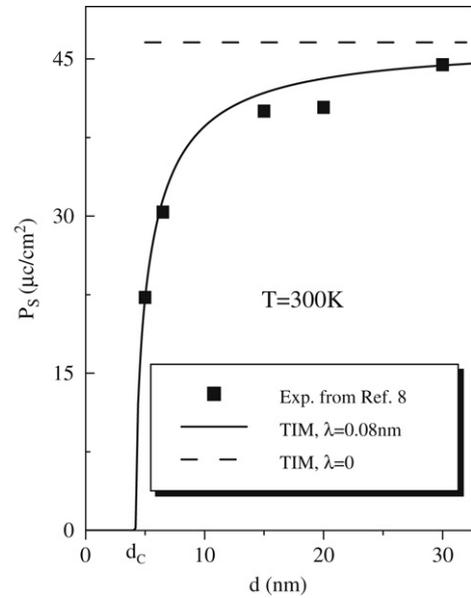


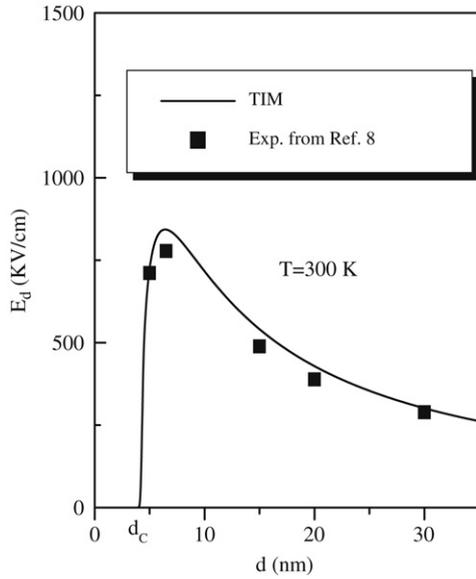
Fig. 1. Thickness dependence of the spontaneous polarization  $P_S$  for  $T = 300 \text{ K}$ . The solid and dashed curves represent the theoretical results for  $\lambda = 0.08 \text{ nm}$  and  $\lambda = 0 \text{ nm}$ , respectively, and solid squares correspond to the experimental data reported in Ref. [8].

## 3. Results and discussion

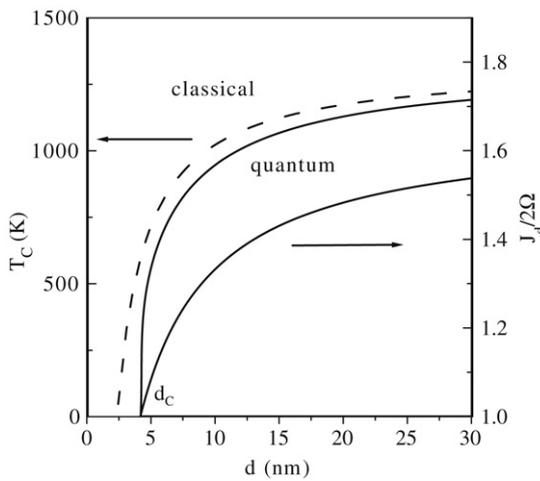
Fig. 1 shows the thickness dependence of the spontaneous polarization  $P_S$  at  $T = 300 \text{ K}$ . Our theoretical results are in good agreement with the experimental data. Note that the  $P_S$  value with  $d = 30 \text{ nm}$  is about  $44 \mu\text{C}/\text{cm}^2$ , which is larger than the BTO bulk value of  $26 \mu\text{C}/\text{cm}^2$ . This enhancement should be attributed to the compressive strain imposed by the STO substrate. Since the intrinsic surface effect is neglected, the spontaneous polarization should be thickness independent for a film with an ideal electrode ( $\lambda = 0 \text{ nm}$ ). For a film with a realistic SRO electrode ( $\lambda = 0.08 \text{ nm}$  [8]), however, the incomplete charge compensation will reduce the spontaneous polarization. Moreover, with the decrease of the film thickness, the spontaneous polarization exhibits a more and more rapid decrease with decreasing film thickness and approaches zero at a critical thickness  $d_c(T = 300 \text{ K}) = 4.2 \text{ nm}$ , indicating that the incomplete charge compensation in a real electrode will assume increasing importance in films with decreasing thickness.

The above polarization behavior originates from the competition between the thickness dependent pseudospin interaction and quantum mechanical tunneling, and consequently it can be explained in a certain microscopic mechanism with the quantity  $J_d/2\Omega$  to scale the quantum effect (this will be discussed below), which leads to the dramatic suppression of ferroelectricity with the decrease of film thickness. Furthermore, the critical film thickness  $d_c$ , below which  $P_S = 0$  for  $T = 300 \text{ K}$ , can be determined from  $\frac{2\Omega}{J_d(d=d_c)} = \tanh\left[\frac{\Omega}{2k_B T}\right]$  by dealing with the Hamiltonian  $H$ .

Fig. 2 lists the experimental  $E_d$  [8] for film thickness between  $5 \text{ nm}$  and  $30 \text{ nm}$  at  $T = 300 \text{ K}$ . The calculated  $E_d$  can again well reproduce the experimental data, confirming the feasibility of the proposed model and the reliability of the theoretical results thereafter. We note that  $E_d$  increases with decreasing film thickness for  $d \geq 6.5 \text{ nm}$ , but steeply decreases with further decrease of film thickness and vanishes at  $d_c$  due to the vanishing electric polarization, which can be explained by the fact that the depolarizing field is affected by both the film thickness and electrical polarization. For  $d \geq 6.5 \text{ nm}$ , the film thickness plays a dominant role, while for  $d < 6.5 \text{ nm}$ , the role of polarization becomes more important.



**Fig. 2.** Thickness dependence of the depolarizing field  $E_d$  for  $T = 300$  K. The solid curves correspond to the theoretical results and solid squares are experimental data reported in Ref. [8].



**Fig. 3.** Thickness dependence of the phase transition temperature  $T_C$  (left horizontal arrow) and  $J_d/2\Omega$  (right horizontal arrow). The dashed line represents our extrapolated thickness dependence of  $T_C$  for the classical case under the approximation  $T_C \gg \Omega/2k_B$ .

By dealing with the Hamiltonian, we obtain the analytical thickness dependence of transition temperature as

$$T_C = \frac{\Omega}{2k_B \arctanh(2\Omega/J_d)},$$

which decreases more and more rapidly with the film thickness and approaches zero at  $d_c(T = 0 \text{ K}) = 4.17 \text{ nm}$  (Fig. 3). It should be noted that  $J_d/2\Omega$ , which varies with the film thickness due to the incomplete charge compensation caused by the imperfect electrode, is used to scale the quantum effect in our calculation within the framework of the TIM. With the decrease of the film thickness, the reduction of  $J_d/2\Omega$  will cause the enhancement of quantum effect and the suppression of ferroelectricity (Fig. 3). The critical thickness, at which  $T_C = 0 \text{ K}$ , corresponds to the case of  $J_d/2\Omega = 1$ . With the decrease of film thickness, the quantum fluctuation gradually dominates over the decreasing polarization interaction, leading to the transition from ferroelectric behavior at  $J_d/2\Omega > 1$  to paraelectric behavior at  $J_d/2\Omega < 1$ .

For classical cases, where  $T_C \gg \Omega/2k_B$ , the thickness dependence of transition temperature can be expressed as

$$T_C \approx T_{C(\lambda=0)} - \frac{8N\mu^2\lambda T_{C(\lambda=0)}/\varepsilon_0\varepsilon_e J}{d}$$

(dashed line in Fig. 3), where  $T_{C(\lambda=0)} = \frac{\Omega}{2k_B \arctanh(2\Omega/J)} = 1323 \text{ K}$  is the transition temperature for BTO film with an ideal electrode. If we extrapolate this result to the low temperature region, we easily obtain the critical thickness  $d_{c1} = 2.4 \text{ nm}$ , in good agreement with the predicted data [4] through the first principles calculation. The above-mentioned relation is in accordance with that derived within the framework of the nonlinear thermodynamic theory by including the effect of the depolarizing field [19,20], where the influence of the quantum mechanism was neglected. In contrast to the classical cases,  $T_C$  and the critical thickness  $d_c(T = 0 \text{ K})$  will remarkably deviate from the classical results under the role of the quantum mechanism.

We further demonstrate the thickness dependence of the dielectric behavior at various temperatures in Fig. 4. It should be noted that the above-mentioned  $T_{C(\lambda=0)}$  is a special temperature point, above which the critical thickness  $d_c \rightarrow \infty$ . The dielectric properties for temperatures below and above  $T_{C(\lambda=0)}$  are completely different. Below  $T_{C(\lambda=0)}$  (Fig. 4(a)), the reciprocal dielectric susceptibility ( $1/\chi$ ) decreases with increasing thickness and approaches zero at a finite critical thickness, above which  $1/\chi$  increases with film thickness. Below the critical thickness ( $P_S = 0$ ), the reciprocal dielectric susceptibility

$$1/\chi = \frac{2\Omega \coth(\frac{\Omega}{2k_B T}) - \frac{J_d}{2}}{N\mu^2/\varepsilon_0}.$$

Thus, the quantum effect is weakened by the increasing polarization interaction with the increase of the film thickness, resulting in the decrease of  $1/\chi$  and its vanishing at  $d_c$ . Above the critical thickness with nonvanishing  $P_S$ , the BTO thin film shows a dramatic increase of its reciprocal dielectric susceptibility due to the increasing spontaneous polarization with the increase of the film thickness.

It can be seen from Fig. 4(b) that, at  $T = T_{C(\lambda=0)}$ , the thickness dependence of  $\chi$  shows a linear behavior. At this temperature, the role of thermo-perturbation exactly overcomes the role of polarization interaction  $J$ , i.e.

$$\Omega \coth\left(\frac{\Omega}{2k_B T_{C(\lambda=0)}}\right) - \frac{J}{2} = 0,$$

resulting in a disordering polarization state for films with any finite thickness. As a result, BTO thin film with any finite thickness will not demonstrate ferroelectric properties at this temperature and  $\chi$  can be expressed as  $\chi = \varepsilon_F + \frac{\varepsilon_c}{2\lambda}d$ . Furthermore, at temperatures higher than  $T_{C(\lambda=0)}$  (Fig. 4(b)), the thickness dependence of  $\chi$  will present a nonlinear behavior and saturate to a constant,

$$\chi(d \rightarrow \infty) = \frac{N\mu^2/\varepsilon_0}{2\Omega \coth(\frac{\Omega}{2k_B T}) - \frac{J}{2}},$$

which resembles the experimental thickness dependence of the dielectric constant for FE (Ba, Sr)TiO<sub>3</sub> thin films [20,21]. In addition, with the increase of temperature, the dielectric susceptibility will decrease because of the polarization disorder induced by the increasing thermo-perturbation.

#### 4. Conclusions

In summary, we have proposed a simple way to investigate the size effect on SRO/BTO/SRO FE ultrathin film capacitors with film thickness fully strained with an STO substrate. We show that BTO ultrathin films between two metallic SRO electrodes lose

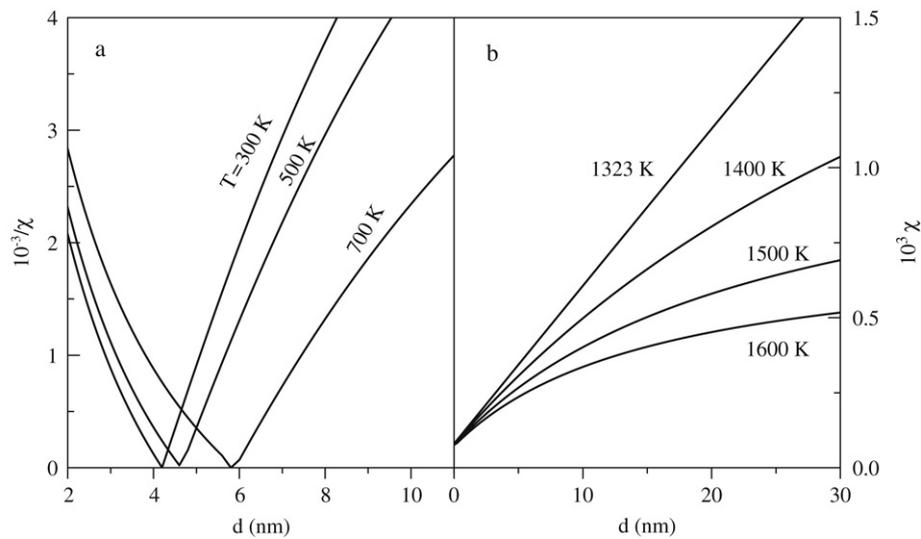


Fig. 4. Thickness dependence of (a)  $1/\chi$  for  $T < T_{C(\lambda=0)}$  and (b)  $\chi$  for  $T \geq T_{C(\lambda=0)}$ .

their FE properties below a critical thickness of about 4.17 nm, which, through our theoretical calculation, can be attributed to enhancement of the quantum effect due to the modification of the polarization interaction  $J_d$  by the effect from the incomplete charge compensation of the imperfect electrode. We also investigate the thickness dependence of the dielectric susceptibility under various temperatures, which shows a behavior similar to that reported for FE (Ba, Sr)TiO<sub>3</sub> thin films. Consequently, with the simple modifications of the parameters in the TIM, the present theoretical treatment can be of great use for the further study of phase transition and dielectric properties in other FE ultrathin films.

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